PARLIN LABORATORY REPORT NO. 889

REFERENCE COPY
NOT FOR CIRCULATION

SUBJECT: ORGANIC FLATTING AGENT FOR LACQUERS, VARNISHES AND SYNTHETIC RESIN COMPOSITIONS.

PERIOD: DECEMBER 12, 1940 TO APRIL 7, 1942

NOTEBOOK NOS. 988, 2006, 2021 and 2025

PREPARED BY: E.F. OEFFINGER

APPROVED BY: R.B. HOLMES

PARLIN LABORATORY REPORT NO. 889

SUBJECT: ORGANIC FLATTING AGENT FOR LACQUERS, VARNISHES AND SYNTHETIC RESIN COMPOSITIONS

INTRODUCTION

The primary purpose of this research project was to develop a polymerized ureaformaldehyde for use as an inexpensive, non-settling flatting agent satisfactory for use in lacquers, varnishes and synthetic resin compositions. This work was covered by major experimental project J-311, dated November 4, 1941. The polymerized ureaformaldehyde resin in question has also been evaluated as a dehydrating agent, decolorizing agent, gas adsorbing material, sanding aide and ion exchange resin.

The recent decision on the part of the management to place long range research work in the background due to urgent war problems has made it necessary temporarily to terminate the work on this research project. Some of the phases of this problem have been completed, some were being actively worked on, and some had not yet been considered. The intent of this report is to place on record the present status of this problem so that future investigators may proceed with this work when time permits.

SUMMARY AND CONCLUSIONS

The polymerized resins evaluated in this work were prepared by treating heated solutions of ureaformaldehyde resin with small amounts of mineral acid accelerator. Sulphuric and hydrochloric acids were found to be the most effective accelerators, and temperatures just below the boiling point of the carrier solvent were generally employed to carry out the polymerization. When examined as flatting agent, these gells were used in mill bases without removing the carrier solvent, but when evaluated in other capacities, this solvent was driven off with heat.

Gelled ureaformaldehyde resin has been found of interest as a flatting agent for "DULUX", "Duco", and enamels. Improvements in settling properties and flatting strength will be required before commercial consideration is given to this type of product, but further effort could undoubtedly overcome these minor objections.

Although dry gelled ureaformaldehyde appears to be an effective gas adsorbing material, we have found it to be impractical for this use as it does not completely remove toxic gases from air, and we know of no method of recovering the resin after such use. Economically it could probably not compete with activated carbon. -

(OVER)

Gelled ureaformaldehyde has been found ineffective as a dehydrating agent, decolorizing agent, sanding aide, and as an ion exchange resin for water purification.

EXPERIMENTAL

The thought behind the preparation of the material with which we are dealing was to polymerize a ureaformaldehyde resin solution with the object of obtaining a gell structure of the same general type as silica gel, (a dehydrating agent) and Santocel (a flatting agent). Both of these materials are silica type hydrogels and are produced by the Davison Chemical Company and the Monsanto Chemical Company respectively. Although it is possible to polymerize a solution of ureaformaldehyde resin by heat alone, this was found impractical due to the time involved, and as a result, most of our work was carried out on the basis of a gelled resin which had been polymerized by means of both accelerator and heat. The various phases of our work are dealt with below.

1. Gelled ureaformaldehyde resin has been found to be an interesting flatting agent for both "DULUX" furniture finishes and lacquers. However, time did not permit the production of a flatting agent which could be considered entirely satisfactory in all respects. In the case of "DULUX" furniture finishes, the chief draw-back was the fact that when satisfactory flatting strength was procured, poor settling results were obtained, whereas when satisfactory non-settling was developed, the flatting strength of the finished material was deficient when compared with Santocel. In the case of pyroxylin finishes, a grinding cycle in excess of that employed with stearate mill bases was found to be necessary, and inferior settling properties in comparison with stearate was experienced. The flatting strength was entirely satisfactory in the case of pyroxylin products.

The Philadelphia Laboratory has examined various gelled ureaformaldehyde resins as flatting agents for varnish and enamels. They have reported them unsatisfactory for use in varnish as a consequence of the high butyl alcohol content, and satisfactory in enamels, with the exception of the high acidity, and in some cases poor flatting strength. It is obvious that all of the objections indicated above could probably be overcome by a continuation of this work.

2. Both water soluble and organic solvent soluble ureaformaldehydes were found to be unsatisfactory as a dehydrating agent.

3. Gelled ureaformaldehyde resin was found to be an interesting gas adsorbent when evaluated with clorine gas, and air saturated with hydrocarbon vapor. The results of this work were covered in Parlin Laboratory memorandum report No. 8 of January 8, 1942. On the basis of our findings, samples of this resin were submitted to representatives of the Chemical Warfare Service for consideration as a gas adsorbent for gas masks. They reported the material unsatisfactory for this purpose as it did not completely remove toxic gases from air Although gelled ureaformaldehyde appears to be a gas adsorbent, we do not anticipate any practical application of this property

4. Gelled ureaformaldehyde resin was found to be unsatisfactory as a decolorizing agent.

5. Gelled ureaformaldehyde resin was found to be unsatisfactory as a sanding aide in lacquer sealers.

6. Recently published work by the Resinous Products and Chemical Company on completely polymerized phenolic resins for use as ion exchange resins for water purification problems, led us to evaluate gelled ureaformaldehyde in this capacity. It was found to be completely ineffective in removing either anions or cations from low concentration solutions of dissolved salt.

7. Our work indicated that straight heat gelled ureaformaldehyde resins were not practical as the gelation time was too long (a matter of days) and the resultant polymerized resin was not rigid enough for satisfactory grinding. As a result of this initial discovery, all subsequent resins evaluated were prepared by the use of a mineral acid accelerator and heat. It is not entirely essential that heat be used but it greatly hastens gelation.

8. It was found that the gelation of high concentration solutions of ureaformaldehyde resins (40-60% solids) produced gels which were so dense that poor grinding and subsequent unsatisfactory settling was experienced. Our most successful results were obtained in the range of 10-25% solids prior to gelation. Of the group of mineral acids evaluated, sulphuric acid and hydrochloric acid appear to be the best accelerators for our purpose. In the case of sulphuric acid a soft easy grinding resin of good non-settling properties was procured, but poor flatting was experienced. In the case of hydrochloric acid, a highly rigid gel was formed which resulted in difficult grinding with subsequent bad settling. Definitely superior flatting results were obtained in the case of hydrochloric acid than in the case os sulphuric.

(OVER)

9. In our initial work no attempts were made to neutralize or remove the acid catalyst used in preparing the gel, and no appreciable detrimental effect was noted in the film quality of the finished product. However, can corrosion was experienced with this procedure. In our later work ammonium hydroxide was used to neutralize the acid catalyst and satisfactory results were obtained by this method.

10. Water soluble ureaformaldehyde and phenolic resin gels were evaluated as flatting agents and found to be unsuitable. In the case of ureaformaldehyde resins, an extremely dense gel was obtained which could not be satisfactorily ground, whereas the phenolic resins produced a soft gummy precipitate of unsatisfactory color.

In evaluating gelled ureaformaldehyde resins as flatting agents in "DULUX" furniture finish, both the RF-5718 and RF-5728 formulas were used. RF-5718 is a product which contains carnauba wax as flatting agent and RF-5728 contains Santocel. The RF-5718 formula has a soluble content break-down as follows:

RC-721 solids	17.15%
G-302	8.05
G-652	1.25
RL-255 (solid)	13.15
H-4	4.30
G-694	6.25
	46.28%

The RF-5728 formula has a break-down composition as follows:

RC-721 solids	16.31%
G-302	7.66
G-652	1.10
RL-255 (solid)	12.56
H-4 (solid)	.40
G-620	3.61
	41.64%

In our work gelled ureaformaldehyde resin was substituted for G-694 in the case of the RF-5718 formula and for G-620 in the case of the RF-5728 formula and compared directly with the standard materials containing carnauba wax and Santocel respectively. All the conclusions based on "DULUX" furniture finish were made on this basis.

In the case of lacquer evaluation the 1661, Type II "Duco" formula was used. A solids breakdown of this material follows:

PX	9.8%
G-356	6.2
G-608	2.2
H-116	3.2
H-22	1.3
G-217	3.5
	26.2%

Gelled ureaformaldehyde was substituted directly for the G-217 in this formula for direct comparison with the standard material.

In all cases the gelled ureaformaldehyde was made into a suitable mill base by grinding in a laboratory mill. It was found that satisfactory grinding could not be obtained in a one quart mill in a reasonable length of time, this fact being previously noted in the case of Santocel mill bases. Therefore, one gallon crocks were used, using a ratio of 2 parts of pebbles to one part of charge, the usual grinding cycle being 48 hours.

In examining gelled ureaformaldehyde as a dehydrating agent, the gel was carefully dried in a 100°C. oven for three days prior to evaluation. The evaluation was made by passing water saturated air at room temperature through a weighed sample of the dry gel for varying periods of time and establishing a curve. In no case was the resin found to adsorb more than 10% of water vapor from saturated air and it is obvious that its efficiency is not great enough to warrant further consideration.

In evaluating gas adsorption, pure chlorine in one case and air saturated with hydrocarbon vapor in another case was passed through a sample of dry gel, and the increase in weight noted. It was found that as high as 48% of chlorine could be adsorbed by a gel prepared from a 30% solution of ureaformaldehyde resin, whereas as high as 28% hydrocarbon vapor could be adsorbed by this same type of gel. This work is more completely covered in Parlin Laboratory memorandum report No. 8 of January 8, 1942, under the subject of Gelled Ureaformaldehyde Resin as a Gas Adsorbent.

In examining dried ureaformaldehyde resin gel as a decolorizing agent, impure dibutyl phthalate was employed and Darco was used as a control. When treated by the standard

(OVER)

testing method which consisted of adding 2% of the decolorizing agent to the impure dibutyl phthalate and heating in an oven at 70°C. for one half hour, it was found that the Darco gave satisfactory decolorizing action whereas none of the gelled ureaformaldehyde resins did.

In examining gelled ureaformaldehyde as a sanding aide, a mill base of this material was prepared and the product was used as a replacement for zinc stearate in 1935, a 21% solids Type I patent sealer. It was found that gelled ureaformaldehyde was very poor in this capacity.

In evaluating resins of this type as ion exchange resins, 10% of the dry gelled resin was added to a one half percent sodium chloride solution using an equal amount of resin with distilled water as a control. After allowing these materials to stand overnight the pH was determined on the treated and untreated water. It was found that treatment with gelled ureaformaldehyde resin tended to make the solution more acidic, but as this increased acidity was also in evidence with distilled water, it was concluded that the gelled ureaformaldehyde is not effective as an ion exchange resin and that the acidity produced was in all probability due to the residual acid accelerator in the resin.

EFO:MCN
4/24/42